SCIENCE FOR GLASS PRODUCTION

UDC 620.22:666.1

NANOTECHNOLOGY IN GLASS MATERIALS (REVIEW)

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Translated from *Steklo i Keramika*, No. 5, pp. 12 – 17, May, 2008.

The status of nanotechnology is briefly examined. It is noted that a quite large number of existing glass materials contain nanostructures and essentially are nanomaterials (nanocomposites). A classification of the nanostructures observed in glasses is given. The nanolevel structure of certain known glass materials is described, and their properties which are due to the presence of a nanophase are presented. Certain glass-based nanocomposites which are obtained today are identified and certain problems of directed synthesis of nanocomposites with a glassy matrix are elucidated.

The term "nanotechnology" is interpreted differently in different sources [1–3]. In the Concept of Development in the Russian Federation of Work in the Field of Nanotechnologies for the Period up to 2010, which the government of the Russian Federation approved on November 18, 2004, "nanotechnology" is defined as methods and techniques which enable the development and controlled modification of objects that include components smaller than 100 nm in at least one direction and that, as a result, acquire fundamentally new qualities which make it possible to integrate these components into fully functioning large-scale systems [4]. "Nano-" (from the Greek ηαηοζ — dwarf, little old man) — is a prefix for forming tenths of a unit, corresponding to the factor 10^{-9}.

In 1974 the Japanese physicist Nogio Tanaguchi was the first to propose a name for the new direction in science and technology — "nanotechnology." He described processes for constructing new objects and materials by manipulating individual atoms, i.e., working with particles one billionth of a meter in size. The birthday of the technology is considered to be December 29, 1959, when the American physicist Richard Feynman first published a work in which he assessed the prospects for miniaturization. In 1986 nanotechnology became known to a wide public. Several monographs written by foreign authors on nanotechnologies have appeared over the last few decades. In works where questions of the history of nanotechnology are considered, the first artificial materials which contain nanoparticles are called colored glasses with colloidal (elementary) color centers [3].

A brief history of the development of nanotechnology is given in [5, 6].

Over the last brief period the analytical firm "Lux Research Inc." identified 14 leading countries out of 50 which are developing nanotechnologies, taking account of the scientific potential, financing, and implementation of advances. It divided the 14 countries into four groups [7]:

USA, Japan, South Korea, Germany (dominant leaders);

Taiwan, Israel, Singapore (small countries but actively developing nanotechnologies);

Great Britain and France (countries with the highest scientific potential but modest implementation of advances);

China, Canada, Australia, Russia, and India (lowest league).

On the basis of citations of Russian "nanopublications" in the world literature, our country is eighth. The works concerning the physics of low-dimensional structures and nanoelectronics which were performed under the leadership of the Nobel Laureate Academician Zh. Alferov [8] are in first place. In one interview he named two promising directions which have a direct bearing on glass:

obtaining various forms of nanocoatings;

obtaining nanoporous glass which selectively transmits oxygen in a room and removes undesirable gases from the room.

Today, the greatest results have been achieved in nanoelectronics and nanobiotechnology [9 – 11].

Nanoparticles in materials science are primarily metals, oxygen, oxides, nitrites, and carbides [12 – 14]. In the last few years even the field of construction materials engineering has encountered this direction, though at first glance this seems paradoxical [15 – 18].

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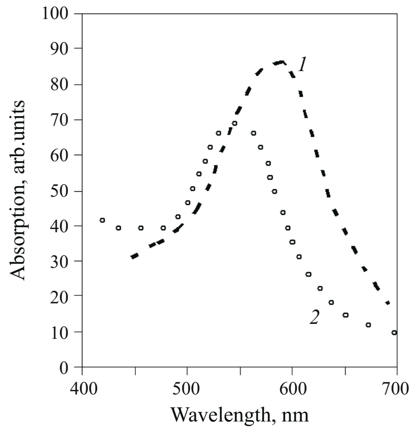


Fig. 1. Optical absorption spectra of glasses with gold nanoparticles with a diameter of approximately 80 nm — red glass (*1*) and 20 nm — yellow glass (*2*) [3].

The investigation of the "achievements" of nature on the level of practical applications and past achievements of science and technology is an important direction in modern "nanoscience." It is obvious that nanostructures existed long before intelligent life appeared on Earth. Many natural processes occur with the participation of nanostructures, i.e., nature was the first nanoengineer. Many conventional artificial materials, including glass, ceramics, and glassceramics, obtained at different stages of the development of civilization, contain nanostructures or possess nanostructural construction. The study of conventional materials with nanoparticles makes it possible to formulate the basic directions of development of nanomaterials science.

Academician of the Russian Academy of Sciences M. Alkhimov notes two directions of motion in the nanoworld:

"Bottom to top" — the development of new materials and molecules according to self-assembly technology, as the most complicated revolutionary path to the development of new materials, and "top to bottom" — the transition from microstructures to nanostructures, as is already done in electronics. This path makes it possible to obtain first-generation nanomaterials which will appear in our life before other nanomaterials.

Among first-generation nanomaterials, nanostructured glass is very promising [19 – 22].

It is not known exactly when man first started using the advantages of nanosize materials. There is evidence that opalescent red and ruby-red glasses containing gold nanoparticles were already obtained in ancient Egypt (approximately 1500 BC), though the mechanism of coloring was discovered only at the end of the 19th century (works of Faraday, Mie). In the fourth century AD Roman glass makers made glass containing metal nanoparticles. The articles made during this era, called the Licurgus cups, are displayed in the British Museum. The cup, representing the death of King Licurgus, is made of glass containing silver and gold nanoparticles [3]. The enormous diversity of beautiful stained-glass windows, made of colored glasses, in medieval cathedrals is explained by the presence of nanoparticles in the glasses.

Today, copper, silver, platinum, bismuth, or other metal nanoparticles are also used for coloring glasses with the aid of special heat-treatment. Glass acquires different spectral characteristics depending on the size of the nanoparticles selected, for example, gold (Fig. 1).

Different colors can also be obtained by coloring glass with silver particles, regulating this process by the amount of colorant introduced, oxidation-reduction and temperature-time conditions of glassmaking, and subsequent heat treatment — "applications."

Approximate Dependence of Glass Color on Silver Particle Size

Particle size, nm	Color
0 – 25	Blue
25 – 55	Green
35 – 45, 50 – 60	Yellow-green
70 – 80, 120 – 130	Brown

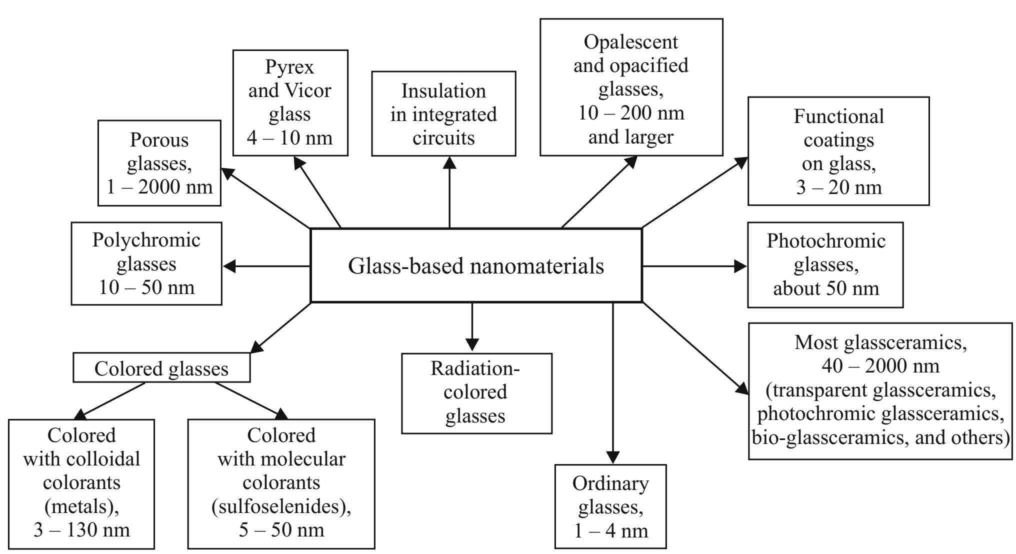


Fig. 2. Nanomaterials based on glass (the approximate characteristic size of the formations is indicated).

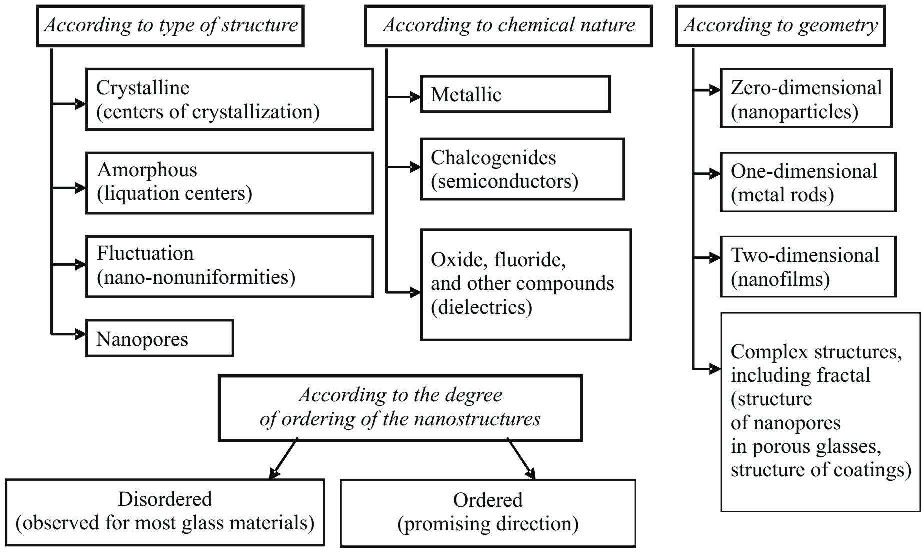


Fig. 3. Classification of nanostructures observed in glasses and glass-crystalline materials.

Many glass materials, especially those developed in the second half of the 20th century, are essentially nanocomposites, since they contain a nanosize component (Fig. 2).

We have made an attempt to classify the nanostructures observed in glasses and glass-crystalline materials (Fig. 3).

Aside from glasses with selective light transmission and photochromic and polychromic glasses, large groups of the following materials should be distinguished: functional coatings, porous glasses, and glassceramics.

Coatings on glass, whose compositions and technologies have been undergoing especially rapid development in the last few decades, impart specific properties to glass: heat-protective, antireflective, electric-heating, strengthening, self-cleaning, and others. Some functional coatings on glass are presented in Table 1.

Coatings make glass not only transparent to light but also a structural material for construction. The exterior side of many modern buildings consists of up to 80% glass. Infrared pictures of buildings show that the losses through concrete or brick walls are higher than through a glass packet with heat-proof glass.

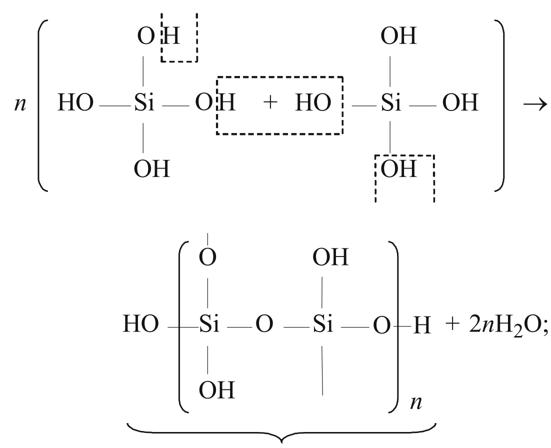
Nanocoatings are obtained by magnetron, cathodic, and plasma sputtering as well as by sol-gel technology, making it possible, in addition, to fabricate monolithic glasses. The initial materials in the sol-gel technology of glassy materials are silicon-organic compounds, whose hydrolysis makes it possible to obtain Si – O – Si bonds, which are the glass-forming base of a silicate coating or monolithic glass.

The main stages of the sol – gel process are as follows:

hydrolysis of tetraethoxysilane in the presence of a catalyst (HCl):

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH;$$

polycondensation of silicon acids with formation of sol particles:



4 – 30 nm in diameter sol particle

coagulation of the sol particles into gel (gel formation):

$$(\text{particle 1}) \equiv Si - OH + HO - Si \equiv (\text{particle 2}) \rightarrow$$
$$(\text{particle 1}) \equiv Si - O - Si \equiv (\text{particle 2}) + H_2O;$$

drying:

monolith (50 – 60°C, hydrostatic compression);

powder (about 100°C);

coating (heat treatment at 400 – 500°C).

Porous glasses, obtained on the basis of liquefying compositions in the system $Na_2O - B_2O_3 - SiO_2$, can also be classified as nanotechnology objects (Fig. 4). They are used as adsorbants, carriers for catalysts, membrane filters, optical and composite materials, and quartzoid glasses, including quartzoid glass fiber. The revival of the glass industry in our country has left this form of production essentially un-

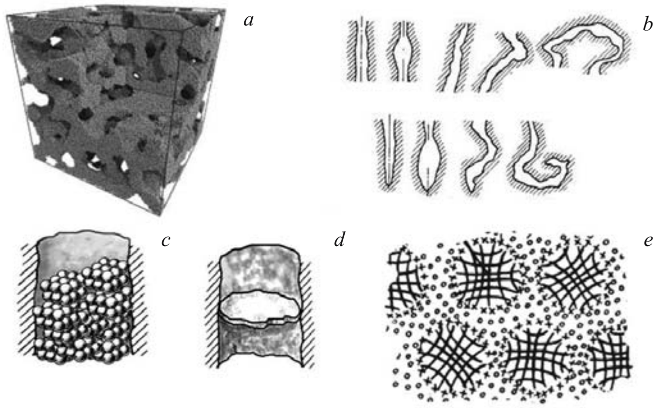


Fig. 4. Type of nanostructures in porous glasses. *a*) spongiform pore structure in porous glass; *b*) types of pores in porous glass (diameter 1 – 2000 nm); *c*) nanodispersed alumina filling pores (diameter 4 – 10 nm); *d*) transverse formation (stratum); *e*) nano-non-uniformity in the glass phase; the smallest possible size of the pores formed between alumina nanoparticles (corpuscular porosity) is about 0.8 nm.

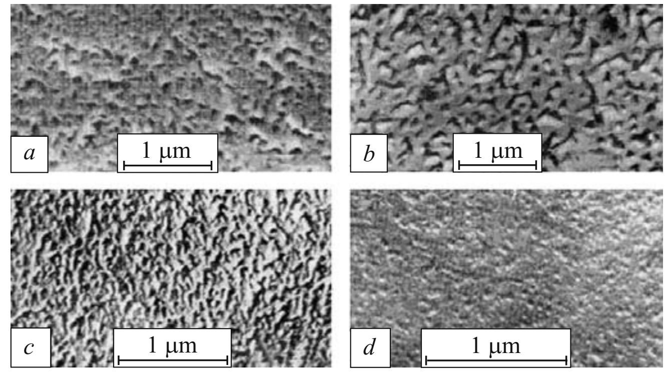


Fig. 5. Different stages of glassceramic formation in glass: *a*, *b*, *c*, *d*) respective average size of the phases (nm): 100 (560°C), 110 (600°C), 30 (700°C), and 60 (initial liquefying glass).

touched. However, scientists have become more interested in such materials in the last few years because of the possibility of obtaining an entire spectrum of different nanocomposites based on them [23, 24].

In glassceramics technology, the onset of the formation of the crystalline phase in the volume of the glass is of a fluctuation nature and occurs at the nanolevel (Fig. 5). Moreover, some glassceramics used in technology and construction contain nanocrystalline phases which impart a series of

TABLE 1.

Type of coating	Structure	Application
	Optical coatings	
Heat absorbing	Semiconductor coatings are represented by SnO_2 nanofilms, modified with Sb, or glassy sol-gel coatings containing IR-absorbing oxides	Construction, transport
Heat reflecting	Consist of nanolayers of metals (Ag, Au, Cu, Fe) — up to 10 nm and translucent nanocoatings (for example, TiO_2) — 20 – 30 nm	Same
Mirror	Thin layers of Al, Ag, or alternating nanolayers with sharply differing refractive indices	Construction, optical instrument building, transport, dielectric mirrors
Translucent	Coating with a thickness of several tens, hundreds nanometers with smaller index of refraction	Optics, construction
Interference (iridescent, luster)	Consist of a 100 – 200 nm thick nanolayer of tin oxide or other oxides	Interference optics, construction, domestic articles
	Electric coatings	
Current conducting	Semiconductor coating, consisting of SnO_2 (10 – 400 nm thick), modified with metals (Sb, Sn) — 100 – 200 nm	Aviation, transport
	Protective coatings	
Strengthening	Essentially all types of coatings exhibit a strengthening effect (“heal” microcracks on the surface of glass) — 100 – 200 nm	Construction, containers, transport
Hydrophobic	Glass surface modified by silicon-organic compounds	Construction, transport
Hydrophobic with “lotus effect”	Coating has a specific nanorelief, which does not allow water drops to remain on the surface	To be used in construction, transport
Superhydrophilic	Nanorelief, which draws water drops into surface channels, flows off as a continuous film	Same
	“Smart” coatings	
Electrochromic	MoO_3 nanolayer (transparent electrode) is deposited on glass, followed by a polymeric electrolyte saturated with Na ions, topped with a second transparent electrode	Optics, to be used in construction
Self-cleaning	Coating consists of anatase TiO_2 nanoparticles modified with ZnO	Construction, systems for removing organic contaminants, transport

TABLE 2.

Glass crystalline materials	System (catalyst)	Phase size,* nm	Composition	Application
High-strength	$MgO - Al_2O_3 - SiO_2$ (TiO_2)	100 – 800	σ_b = 240 – 350 MPa Microhardness 11 GPa	Rocket and aircraft construction, radio electronics
Transparent heat-resistant, radio transparent	$Li_2O - Al_2O_3 - SiO_2$ (TiO_2)	10**	Transparent CLTE = (– 50 ... + 20) × 10^{-7} K^{-1}	Space, laser technology, astro-optics, solar batteries
Photochromic glassceramics	$Li_2O - Al_2O_3 - SiO_2$ + Ag (TiO_2)	10 – 150	Selectively crystallize	Microelectronics, optics, polygraphy, space technology
Bio-glassceramics	$CaO - MgO - SiO_2 - P_2O_5$	500 – 1300	Compatible with biological tissues	Dental and bone prostheses
Construction glassceramics	Different systems	100 – 300	σ_b = 220 MPa Microhardness to 9 MPa Wearability 0.05 g/cm^2	Construction, mining, chemical industry

* The phase size is a ballpark figure.

** According to some data, 6 – 100 nm.

unique characteristics to these materials (Table 2). For example, the size of the crystalline phase in transparent glassceramics is about 10 nm. The fact that the metastable microliquation occurs during the initial period, likewise at the nanolevel, is a favorable factor during crystallization.

Even this brief communication shows the entire arsenal of glass materials with a nanocomponent — obtained accidentally in antiquity or by controlled synthesis in our time, but they were not called nanomaterials. Without these glass materials there would no Kremlin stars, light technology, art or jewelry glass, and such extensive use of glass in construction.

What does the future hold? In what directions should research be conducted? Why is there such a diversity of glass materials with a nanocomponent?

In the first place, the formation and longevity of nanoobjects depends on the medium. After all, no matter how much a material is ground, the dispersity decreases to a definite limit after which the reverse process — aggregation — starts, since nanoparticles are metastable and very active [25]. The main methods for obtaining nano-objects are presented in a number of works [6, 26]. A glass melt is a highly viscous medium, impeding aggregation of the particles, for example, crystallization nuclei, formed in it as a result of concentration fluctuations.

In the second place, glass compositions are extremely diverse. There is virtually no element in the periodic table, including gaseous, halides, and rare earth, that would not be used in glass and would not impart prescribed properties. This determines the extensive field of work, since nanoparticles form not only the properties of nanomaterials but also the special characteristics of the matrices which contain them.

In the third place, glass is very sensitive to external perturbations at the "nano" level and especially to different types of radiation in the entire range of temperature – time interval from melt to the solid-state:

short wavelength — x- and gamma rays (induction color centers arise);

UV radiation (centers of crystallization are formed in photochromic glasses and glassceramics).

The development of nanotechnology is making it necessary to approach the technology even of known materials differently. Today, elements of nanotechnology have already been used to develop nonlinear-optical nanocomposites based on oxide glasses [20, 27], glass fibers reinforced with nanostructures [28], coatings made of nanostructural materials, light-emitting diodes [29], and other glass materials. The very large heat effect during combustion of alumina nanoparticles has already been used in the technology of certain materials to decrease energy consumption [12, 28, 30].

Certain problems in fabricating existing glass materials have already come to light as a result of knowledge about nanotechnology. For example, it has been found that for laser glasses there is a limit on the saturation with neodymium nanoparticles and for a nanoporous glasses — the process of obtaining highly uniform initial glass to ensure metastable liquation at the nanolevel — stresses appear between a nanocoating and the material, though for glasses it is generally known that many coatings strengthen glass, healing surface microcracks.

With the improvement and expansion of the assortment of glass-based nanomaterials, including for use in construction, the facts that, first and foremost, research is of an interdisciplinary nature and, second, special equipment is required must be taken into account. Without unique equipment it is impossible to take a serious step and reach a higher level in materials engineering.

There are fears for mankind should be heeded. The problem is that nanoparticles can contaminate the environment

with highly toxic products of decomposition. "Nanoecology" is already talked about today [31, 32].

Nanoparticles can not only be toxic, explosive or combustible but they can self-organize into very complex structures [33], which opens up a path to creating nanoscopic mechanisms that can radically change life on Earth [34, 35].

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